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This report describes progress in the experimental program to measure reaction rates for the following reactions: (1) $HCl + e \rightarrow H + Cl^-$ (2) $K + Cl \rightarrow K^+ + Cl^-$ (3) $K^+ + e + M \rightarrow K + M$. Measurement of the rate for (1) has been complicated by the large rates for clustering reactions (4) $Cl^- + HCl + M \rightarrow (Cl \cdot HCl)^- + M$. The equivalent attachment coefficient for the first cluster formation ($n^* = 1$) is given as a function of E/p. Performance of a crossed molecular beam apparatus for measurement of the energy dependence of collisionial ionization of potassium and atomic chlorine (2) is described. The experimental technique to be used to

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measure three body recombination in potassium is described. This technique utilizes a laser induced, two step photoionization process which has been demonstrated in cesium.

ABSTRACT

This report describes progress in the experimental program to measure reaction rates for the following reactions:

(1) $HCl + e \rightarrow H + Cl^-$

(2) $K + Cl \rightarrow K^+ + Cl^-$

(3) $K^+ + e + M \rightarrow K + M$

Measurement of the rate for (1) has been complicated by the large rates for clustering reaction

(4) $Cl^- + HCl + M \rightarrow Cl^- \cdot (HCl)_n + M$.

The equivalent attachment coefficient for the first cluster formation (n = 1) is given as a function of E/p. Performance of a crossed atomic beam apparatus for measurement of the energy dependence of collisionial ionization of potassium and atomic chlorine (2) is described. The experimental technique to be used to measure three body recombination in potassium is described. This technique utilizes a laser-induced two-step photoionization process which has been demonstrated in cesium.

1.0 NEGATIVE ION CLUSTER FORMATION IN HCl.

This part of the report will be limited to a discussion of cluster ions of the type $Cl^- \cdot (HCl)_n$ produced as Cl^- ions drift through a background gas of nitrogen or air under the influence of a weak electric field.

A schematic diagram of the apparatus in shown in Fig. 1. Photoelectrons are ejected into the drift region by illuminating a 2 cm^2 sensitized area on the cathode with uv radiation. The photoelectron current in vacuum ($p < 10^{-5}$ Torr)

for a freshly prepared copper iodide coating, or for one sensitized by a glow discharge in hydrogen, approaches 10^{-7} A. The emission current dropped upon admission of gas, however, and stabilized at $\sim 10^{-9}$ A. The primary negative ions are generated by collisions of the electrons with neutral molecules. The average electron energy is kept low so that ionization can be neglected. Negative ions formed in the 2.6 cm drift space, where a nearly uniform electric field is maintained, may pass through an orifice (diam = 0.34 mm) into the mass analysis region.

The negative ions are focused and accelerated by an arrangement of cylindrical lenses. The quadrupole rods and body are biased at +6 and +40 V, respectively, relative to the grounded drift tube housing. The lense potentials are set for maximum signal detection and are not changed during the course of a run. The ions selectively transmitted through the quadrupole are then accelerated to the first dynode of an 18 stage Johnston's Laboratory multiplier, whose pulse output is amplified and counted by an appropriate scaler.

The $HCl-N_2$ gas mixture is supplied and analyzed by the Airco Industrial Gas Company. The relative concentration of HCl to N_2 was 730 ppm $\pm$ 3%. The total gas pressure is measured by a Texas Instruments quartz spiral manometer.

The data from the experiment are recorded as relative ion count rates as a function of E/p at the fixed total pressure p. It is assumed that the electron flux leaving the cathode is uniform over an area large compared to the anode orifice area. This assumption is justified by the use of the photoelectron source and allows the effects of lateral diffusion to be neglected. Longitudinal diffusion will also be neglected.

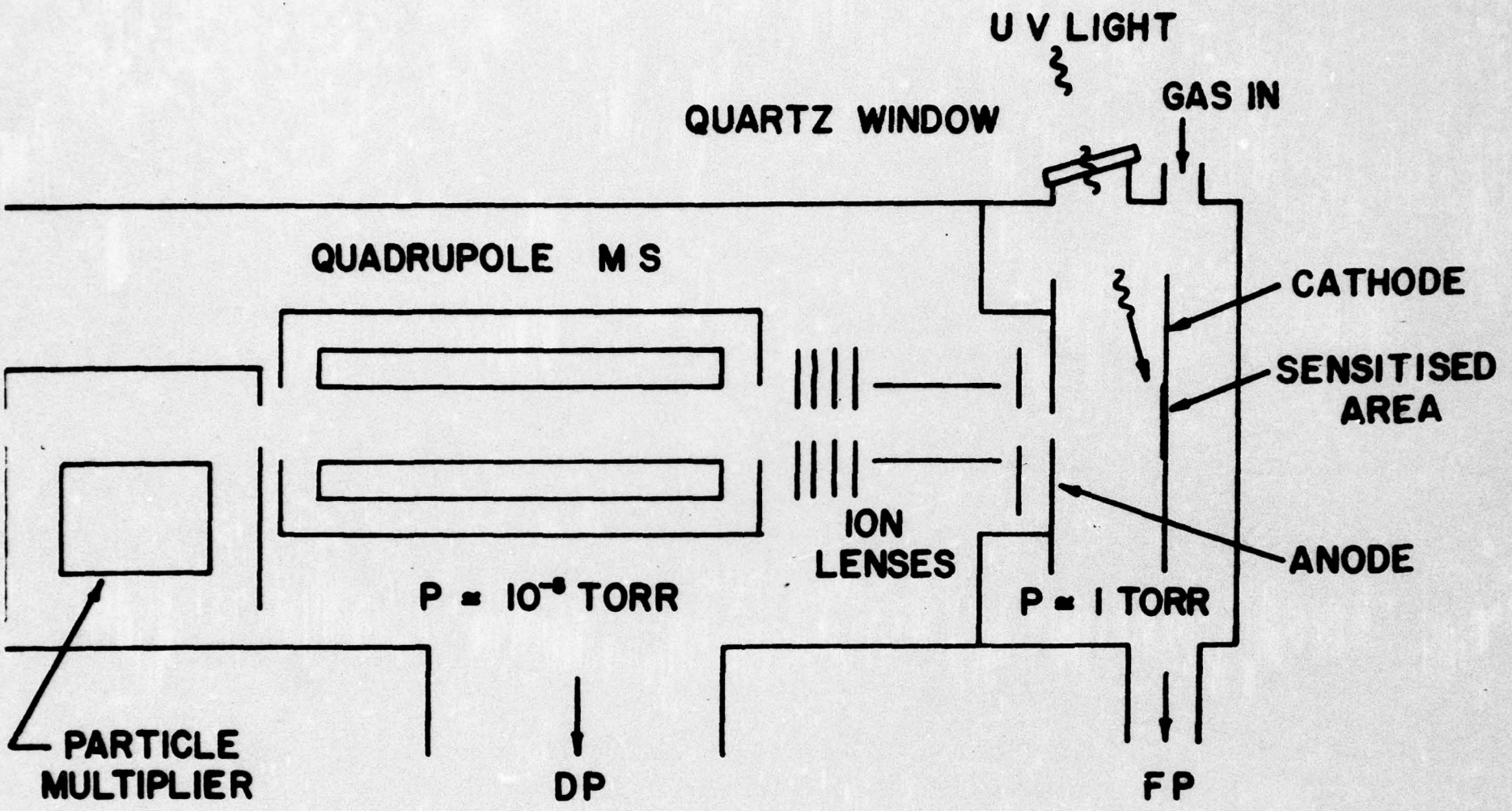

Fig. 1 Drift Tube Apparatus.

After gaining sufficient energy, some electrons undergo the dissociative attachment reaction,

$$e^- + HCl \xrightarrow{k_1} H + Cl^-, \tag{1}$$

to form the primary negative ion observed. The primary ion may have subsequent collisions with an HCl molecule to form a cluster molecule

$$Cl^- + HCl + M \xrightarrow{k_2} HCl \cdot Cl^- + M, \tag{2}$$

where M denotes a third collision partner necessary to stabilize the cluster. In this case the small HCl concentration makes a nitrogen molecule the most likely third body. Higher order clusters may be formed in reactions analogous to reaction (2), however these will be neglected due to the small number observed under our experimental conditions.

The rate equations describing the steady-state number density for the charge carriers are given by

$$v_e \frac{d[e]}{dx} = k_1 [HCl][e] \tag{3}$$

$$v_1 \frac{d[Cl^-]}{dx} = k_1 [HCl][e] - k_2[HCl][Cl^-][N_2], \tag{4}$$

$$v_2 \frac{d[HCl \cdot Cl^-]}{dx} = k_2[HCl][Cl^-][N_2], \tag{5}$$

where the brackets [] denote the number density of a species, k_1 and k_2 denote the rate coefficients for reactions (1) and (2), respectively. v_e, v_1, and v_2 are the drift velocities of electrons, the primary negative ion Cl^-, and the secondary negative ion $HCl \cdot Cl^-$.

For convenience we now define an attachment coefficient η so that

$$\eta_1 = k_1 [HCl]/v_e, \tag{6}$$

and

$$\eta_2 = k_2 [HCl][N_2]/v_1. \tag{7}$$

We also define the flux of electrons, Cl^-, and $HCl \cdot Cl^-$ past an arbitrary plane parallel to the drift tube electrodes by $J_e = v_e[e]$, $J_1 = v_1[Cl^-]$, and

$$J_2 = V_2 \, [HCl \cdot C_1^-].$$

$[HCl \cdot Cl^-]$.

With these definitions the solutions to the differential equations (3) - (5) are given by

$$J_e/J_o = e^{-\eta_1 x} \tag{8}$$

$$J_1/J_o = \frac{\eta_1}{\eta_1 - \eta_2} \left(e^{-\eta_2 x} - e^{-\eta_1 x}\right) \tag{9}$$

$$J_2/J_o = \frac{1}{\eta_1 - \eta_2} \left(\eta_2 (e^{-\eta_1 x} - 1) - \eta_1 (e^{-\eta_2 x} - 1)\right) \tag{10}$$

These relations can then be used to analyze the experimentally determined count rates.

Typical data are shown in Fig. 2. The maximum on the cluster ion count-rate curve below 0.5 Volt is a real physical effect we have observed over a wide range of pressure and E/p - values. A satisfactory explanation is yet to be found. For this reason we shall analyze only the data above 1 volt corresponding to $E/p \geq 0.5$ Volt/(Torr · cm).

If we assume both $\eta_2 d$ and $\eta_1 d \ll 1$, we obtain, by taking the ratio between Eqs. (10) and (9),

$$\eta_2' = \frac{2}{d} \frac{N_2}{N_1} \tag{11}$$

where d is the electrode separation. In this treatment of the data it is implied that both the parent and cluster ions are detected with the same probability at a given E/p.

The coefficient η_2 is important since the quantity $\eta_2 dx$ represents the <u>probability</u> of forming one cluster ion as one Cl^- ions drifts a distance dx along the applied electric field. The results using Eq. (11) are displayed in Fig. 3. For comparison we have also included a more accurate calculation solving explicitly for η_2 from the ratio between Eqs. (10) and (9). By using published data[1] for η_1, we obtain the values marked with squares (□) in Fig. 3. The agreement is good at high E/p values. In the region

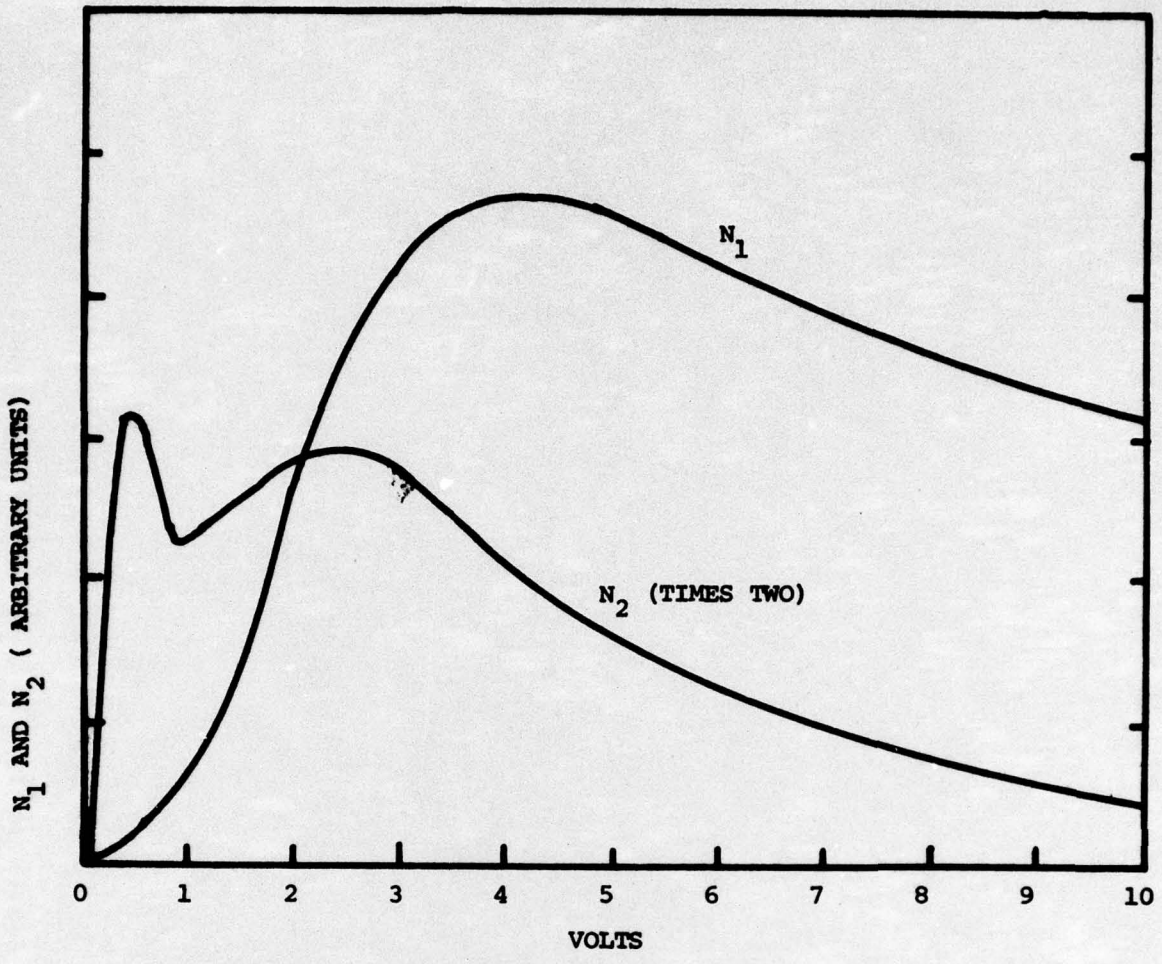

Figure 2. Observed count rates of Cl^- (N_1) and $Cl^-\cdot(HCl)$ (N_2) as a function of applied voltage. The total pressure was 0.8 Torr. The curve for the cluster count rate has been multiplied by a factor of 2 to demonstrate the structure at low voltages.

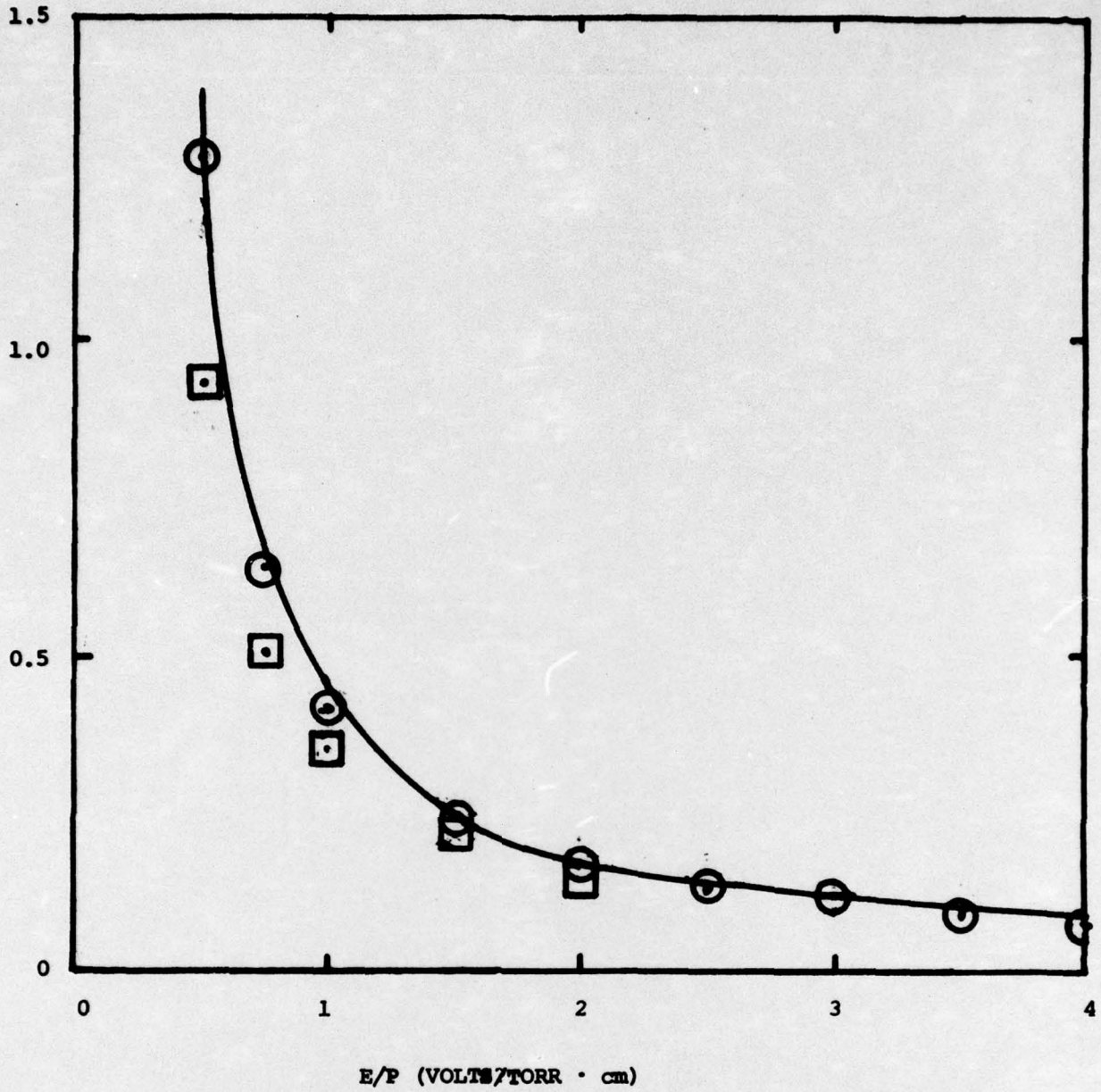

Figure 3. The circles (○), show the attachment coefficients η_2 as calculated form Eq. (11). The squares (□) were obtained using Eq. (12) and the data of Christophoron et al. (ref. 1) for η_2.

of low E/p the assumption of $\eta_2 d \ll 1$ is no longer valid.

2.0 ION PAIR FORMATION IN K - Cl COLLISIONS.

Collisional ionization of potassium and atomic chlorine is thought to be a significant production mechanism for Cl^- in rocket plumes. Measurement of the cross section for

$$K + Cl \rightarrow K^+ + Cl^- \tag{13}$$

using a crossed beam technique is part of the experimental program being pursued under the auspices of this grant.

Figure 4 is a schematic diagram which illustrates the principles of the experiment. A beam of potassium atoms of selected velocity intersects a beam of chlorine atoms in an electric field between two detectors. If a collision occurs between K and Cl with enough energy to produce an ion pair, the resulting K^+ and Cl^- will be attracted to opposing particle multiplier detectors. The cross section for the reaction is a measure of the probability of the reaction proceeding in any collision, and is simply related to the count rate in either detector, assuming that the beam densities and velocities are known.

Nozzle beam techniques will be used to produce an aerodynamically accelerated beam of potassium atoms of high intensity which is nearly monoenergetic.

Figure 5 shows the nozzle assembly as we have modified it to produce the potassium beam. Potassium vapor and helium are mixed in the heated nozzle chamber. The potassium vapor pressure is determined by the reservoir temperature, T_R. The mixture flows through the nozzle in viscous flow so that both components have a velocity,

$$u = (2\bar{C}_p T/\bar{m})^{\frac{1}{2}}, \tag{14}$$

where C_p is the mean specific heat, T the temperature of the nozzle, and $\bar{m}$ the mean mass of the gas mixture defined as

$$\bar{m} = (m_1 P_1 + m_2 P_2) \; / \; (P_1 + P_2), \tag{15}$$

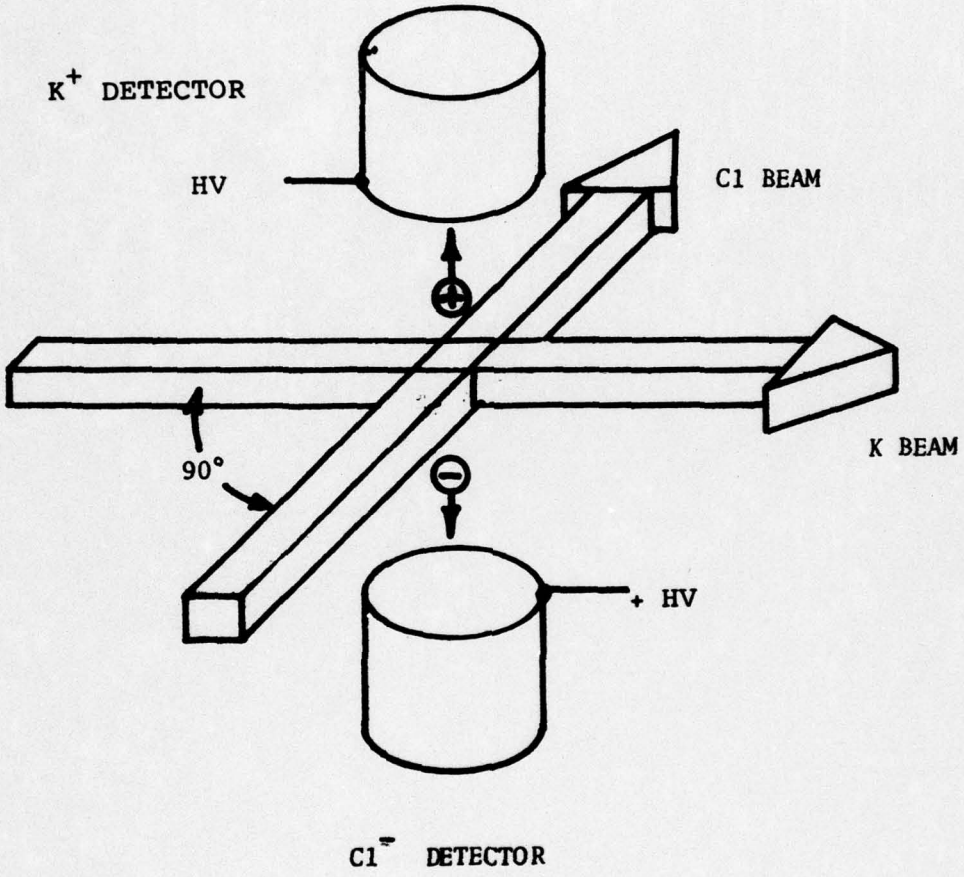

Fig. 4 COLLISIONAL IONIZATION EXPERIMENT

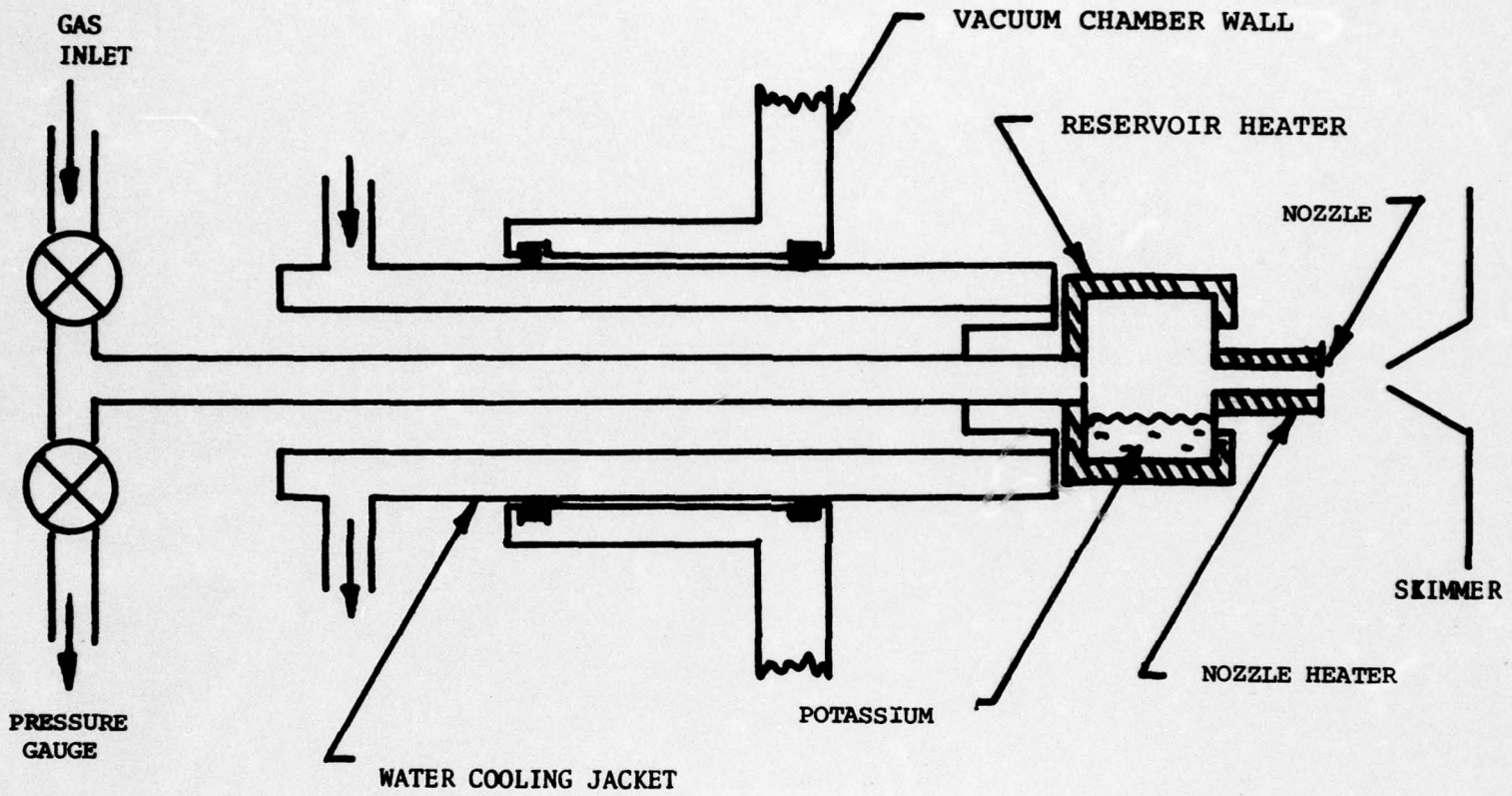

FIG. 5 NOZZLE ASSEMBLY

where P_1 and P_2 are the partial pressures of potassium and helium. As demonstrated by Larsen, Neoh, and Herschbach[2], K beam velocities from thermal to 4.5 x 10^5cm/sec are achieved by controlling both the gas mixing ratio and the nozzle temperature. Center-of-mass energies of 2.5 eV for the K + Cl system should be readily available. If collisional ionization is an important mechanism in plumes below 10^4 ^oK (1 eV), the reaction rate should be significant at 1 to 2.5 eV. The threshold energy for the reaction is approximately 0.8eV.

During this reporting period the oven source shown in Figure 6 was built and tested. It was found that the long tubing from the potassium reservoir to the nozzle was difficult to heat uniformly due to the confined space available in the nozzle source apparatus which we are modifying. Furthermore, the potassium apparently is effectively pumped by the stainless steel walls of the tubing. Ultimately, the intermediate heater arced to the water jacket and burned a hole in it allowing water in and ruining the assembly. The revised design of Figure 2 has been completed and successfully brought up to a nozzle temperature of 1200^oK. The fluxes of both fast and slow potassium atoms are measured with a hot tungsten wire surface ionization detector.

Chlorine Beam Source

Since chlorine is normally a diatomic gas, it must be dissociated to produce a beam of chlorine atoms. We are using a chlorine resistant Mullite oven heated by a resistive element bonded to the oven tube by a castable ceramic, as shown in Figure 7. Also shown is the arrangement for measuring the fraction of atomic chlorine in the beam from the oven. The beam is modulated by a chopper wheel at 100 Hz to permit ac lock-in detection of the ions formed by electron bombardment in the ionizer and thereby effectively discriminate against ions formed in the background gas. The product ions are mass analyzed

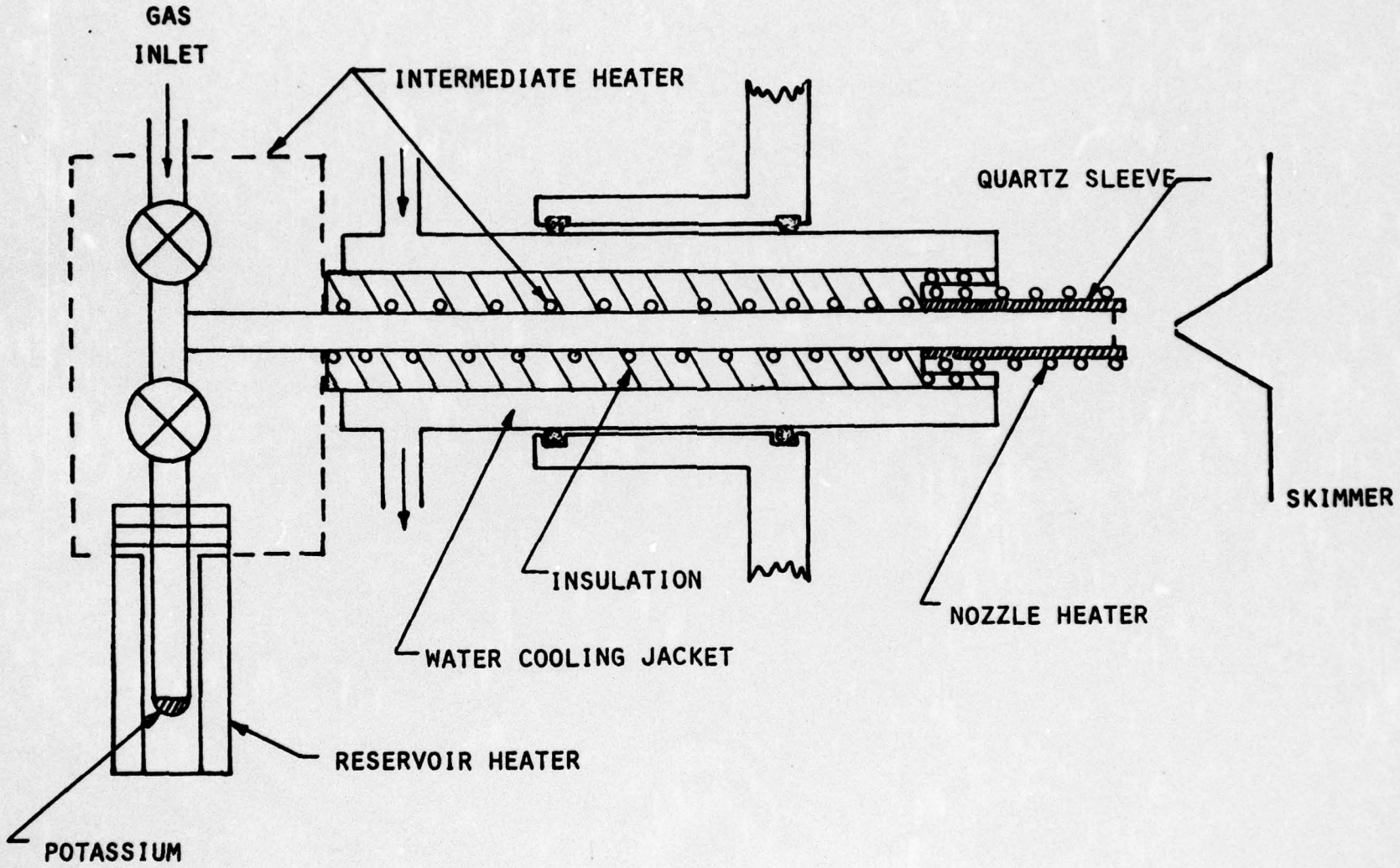

FIG. 6 - NOZZLE ASSEMBLY

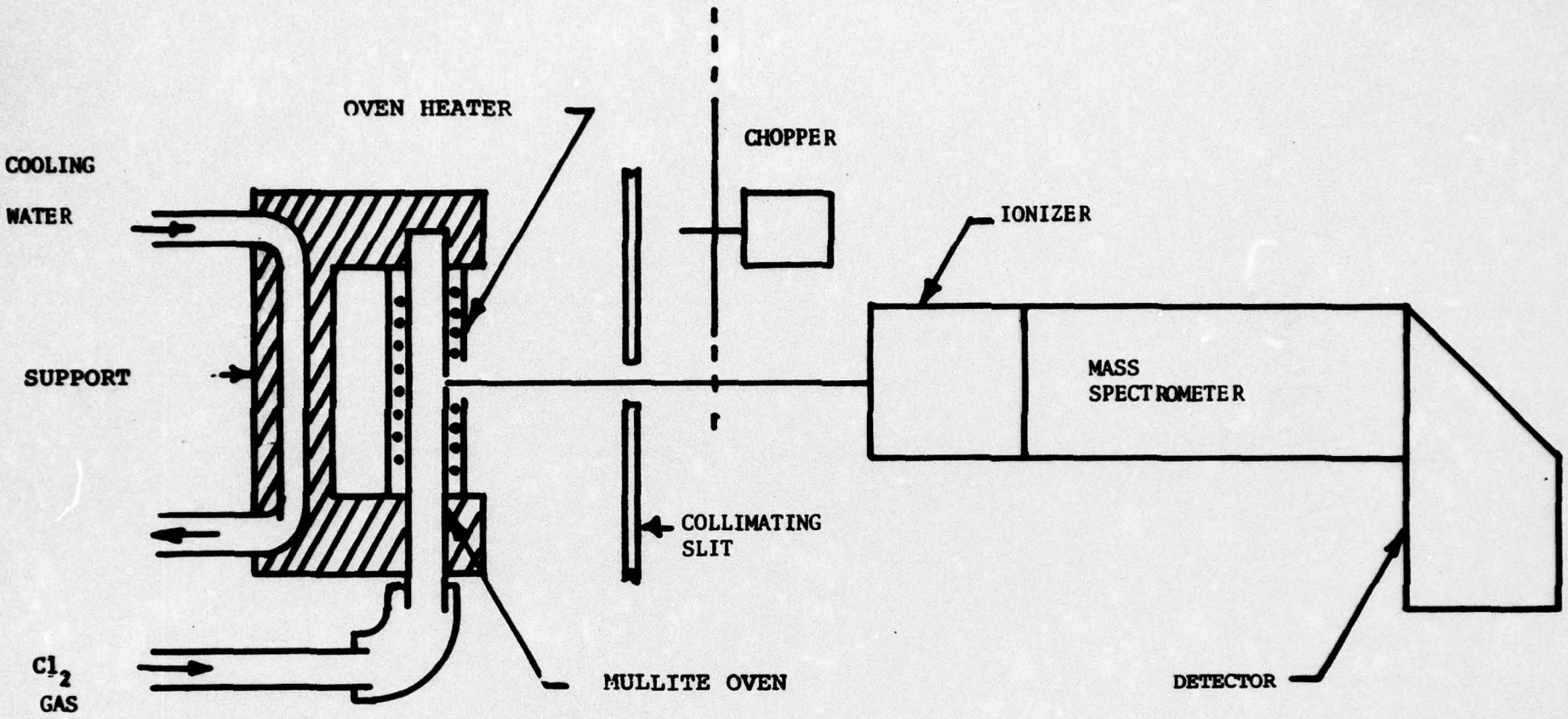

FIG. 7 CHLORINE ATOM SOURCE

and detected with an electron multiplier operated in a current mode.

The present oven source is a considerable improvement over a previous design using a graphite tube. It was found difficult to satisfactorily heat the tube due to its high thermal conductivity. With the present oven we find about 30% dissociation at an oven temperature of 1200°K. Experiments are in progress to measure this dissociation fraction as a function of oven temperature. As anticipated, difficulties are being encountered due to the extremely corrosive nature of atomic chlorine. Even so, it seems probable that the equipment will operate satisfactorily for 50-100 hours between clean-ups.

The ionization cross sections for $e + Cl_2$ and $e + Cl$ are essential to this technique of measuring the fraction of chlorine atoms in the beam. Since measurements of these cross sections were unavailable, we have spent some effort to measure them. Measurement of the cross sections for $e + Cl_2 \rightarrow Cl^+_2 + 2e$ and $e + Cl_2 \rightarrow Cl^+ + Cl + 2e$ were reported last year. As a by-product of the measurement of oven characteristics, the cross section for $e + Cl \rightarrow Cl^+ + 2e$ will be measured.

3.0 THREE BODY POTASSIUM ION RECOMBINATION. ($K^+ + e + M \rightarrow K + M$)

During this grant period the pulsed Xenon-ion laser (2315 Å) described in the last annual report was used in an attempt to produce a potassium plasma by direct photoionization. The laser beam was directed through quartz windows into a heated stainless steel oven containing potassium and helium. The decay of the plasma was measured by observing the characteristic emission lines of the atomic potassium spectrum produced by the recombination of electrons with potassium ions. This preliminary experiment has not yet produced usable results, primarily due to interference of ions produced from the walls of the oven by scattered light from the laser pulse.

An alternative method of ionization, suggested by results of an experiment

performed in cesium, which will avoid the scattered uv photons is now under investigation. In this work a helium-filled cell with a small concentration of cesium was illuminated with monochromatic light from a nitrogen-pumped dye laser. The vapor filled cell was observed at normal incidence to the laser beam with a monochromator. When the dye laser was tuned to 4554 Å, the wavelength corresponding to the 6S-7P transition in cesium, a strong line was detected at 3889 Å with a decay time 100 times longer that the laser pulse.

The most probable explanation for the 3889 Å emission is that some of the Cs atoms undergo a two-step photoionization process via the 6S - 7P transition. Electron-ion recombination then occurs into highly excited states, which cascade down toward the ground state. The 3889 Å line is emitted by those atoms undergoing the 8P - 6S transition. Since preliminary measurements with electrodes in the cell showed that the appearance of the 3999 Å line was definitely associated with the production of ions, this line will provide a convenient way to monitor the recombination process.

We are in the process of building a cell to make similar measurements in potassium. Provision will be made for ion collection and for changing buffer gases and buffer pressures to determine the three body recombination rate.

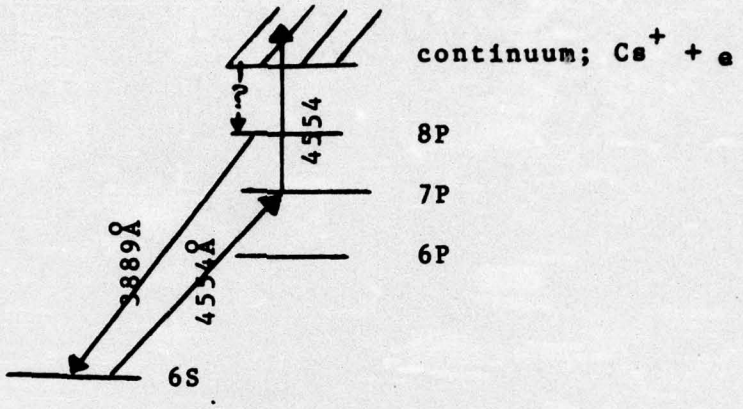

Figure 8. Simplified Cesium term diagram.

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